Fast batch to continuous solid-liquid extraction from plants in continuous industrial extractor

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Abstract

In this work, a study about solute continuous extraction from vegetable matrix is undertaken. An industrial apparatus is used and the problems are to identify information to be acquired in order to process implementation. To this end, a batch study was carried out to obtain the extraction kinetics, as well as a study of the matter behaviour under pressure and a study of raw plant transport. Finally, to couple these elements makes it possible to represent the extraction yields according to time in the apparatus. A methodology for the change from batch to continuous extractor based on laboratory tests is proposed.

Keywords: Solid-liquid extraction, leaching, active principle, continuous industrial extractor, batch to continuous, fast process development

1 Introduction

Solid-liquid extraction is based on the diffusive transfer of solutes from a solid to a surrounding solvent [1]. It represents an important part of many industrial processes. Extraction from plants is common in the perfume industries, in the pharmaceutical sector, in the food and human nutrition field. It allows to obtain some phyto-extracts (e.g. edible or industrial oils, oleoresins, pigments, and natural pharmaceuticals). Continuous counter-current extraction or leaching processes are widely used instead of mechanical pressing processes. The use of a solvent leads to a selective extraction. Schwartzberg [2] described some of the common continuous extractors used in food industry. These processes can answer the following constraints: minimize solvent use and decrease both solute and solvent recovery costs.

From vegetable matrix, considerable interest has been shown in secondary metabolites such as fragrances, pharmaceuticals and flavours. Plants produce a wide variety of secondary metabolites that do not play any vital physiological function. They are present in small quantities, and then several tons of plants are necessary to extract a few grams. To exploit plant material resources, extraction techniques have been developed to obtain such secondary metabolites for commercial purpose. There are three main types of extraction techniques involving the use of solvent, steam or supercritical fluids [3]. Da Costa, Margolis, Benner, and Horton [4] compared supercritical fluid extraction and pressurized fluid extraction with conventional solid-liquid extraction for their efficiency in extracting flavanones and xanthones. But due to temperature constraint on product degradation and heating cost, cold extraction is still widely used.

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The extraction yield of compounds from plant materials is influenced by the conditions under which the process of liquid-solid extraction is carried out [5]. The choice of solvent, of extraction temperature and of mechanical action (pressure, agitation…) is important. Moreover, the vegetable matrix has a complex microstructure formed by cells, intercellular spaces, capillaries and pores. Solute influences extraction by its molecular structure, its size, its localisation and its link with others components. The chemical characteristics of the solvent and the diverse structure and composition of the natural product ensure that each material-solvent system shows different behaviours, which cannot be easily predicted [6]. In an industrial context, this leads to the necessity of developing fast and reliable methods to implement this operation [7]. The key point is to acquire in small batch experiments the information required to optimize the working of a given industrial continuous apparatus.

In the present work, the solid-liquid extraction is studied in an industrial Vatron Mau unit which is a continuous single-screw counter-current extractor. The extractor treats large solid loads, which have different potentials, in order to extract a weak solute amount. The difficulty is to obtain the same yield in the Vatron Mau unit as in batch. Moreover, the contact between solid and liquid phase is different. Advantages over the conventional batch extraction methods include a decrease in solvent consumption and shorter handling time. This study will be integrated in a classical pharmaceutical industry methodology as the first step of the batch to continuous process transfer.

2 Material, experimental device and results

For confidentiality reasons, names of the plant used and molecules extracted are not revealt. In various figures, values are multiplied by a factor X.

2.1 Plant

The raw material is received in bundle form of dried and compacted plant. Before the extraction, the raw material is just unpacked but not grinded. Average density of plant unpacked bed is 0.2 g cm^{-3}. A plant amount absorbs 1.5 times its weight in solvent volume.

The solute, from secondary metabolites, is imbedded into the plant cells under free form. Its concentration depends on climatic growing, gathering, packaging and storage conditions. So, the plant quality changes from a production lot to an other. Average solute concentration is the range of gram per kilogram of raw material. This plant potential is obtained by 6 extractions in batch of a raw material sample, at ambient temperature, during 1h with fresh solvent each time.

There are many general techniques to analyse solute such as high-performance thin-layer chromatography, gas chromatography, supercritical fluid chromatography, and high-performance liquid chromatography (HPLC). In this study, analyses are performed by HPLC with a system from Thermo Finnigan (Paris, France), Serie AS1000XR, with a pump Serie P1000XR and a Waters column (symmetry$^{®}$ C18, 3.9 mm x 150mm) with a UV detector (Thermo Finnigan, France), Serie UV2000. The volume injection is 20 µL. The calibration curve is obtained using standard pure crystal coming from Pierre Fabre, Plantes & Industrie, France. The reproducibility of the analytical methods and the repeatability of the analysis were assessed by evaluating the peak area variation of pilot solution distributed regularly between the samples.

2.2 Vatron Mau experiment

2.2.1 Vatron Mau description

The Vatron Mau continuous counter-current extractor, shown in Fig.1 and Fig. 2, consists of a single-screw housed in a C-shaped barrel. The screw rotates continuously in one direction. 'Counter-current' means that the direction of solvent flow is opposed to the raw material one. The fresh solvent is in contact with the material depleted in solute, whereas the fresh plant is in contact with the extract which is enriched in solute.

The screw conveyor (5) is installed within an inclined 3° relative to horizontal housing. The diameter screw is 298 mm and the screw pitch is 200 mm. The screw is driven by an external motor (6) with a speed controller. The barrel is a 8 m long bored plate which allows the solvent flow. Raw material is fed into the lower end of the barrel in section 1 and carried upwards by screw rotation. The rotation speed, when the extractor is empty, is ranging from 0.1 to 1 rpm. The time for the feed to travel to the discharge-end from the feed-end is called the residence time. It is ranging from 0h40 to 6h20. Solvent is fed into the top by tube (2), directly on the retention tank. The extractor is composed of 8 compartments. A retention tank (9), average capacity of 67 L, with one centrifugal pump (10), 10 m^3 h^{-1} maximum flows, corresponds to one compartment called 'stage'. But, it is not an equilibrium stage. The pump ensures the solvent recirculation on the surface of material tanks to a dispersion nozzle. The bulk phase is separated to marc by barrel, which behaves as filter-media, and it is collected in retention tank. The solvent transfer from a tank to the other is carried out by overflow. The last stage, number 8, is a draining stage. Temperature sensors and heat exchangers (11) to plates are regularly distributed along extractor on stage n°1, n°2 and n°6.

The Vatron Mau is a closed unit. The atmosphere inerting can be carried out by nitrogen whenever the solvent vapours are explosive with air. Glazed inspection lids on the top and the sides of extractor make it possible to observe the process.

2.2.2 Experimental conditions

Experiments were carried out in non classical conditions which differ from the industrial usual ones. At the beginning, tanks are filled to capacity of solvent. Fresh solvent was introduced only on the first stage to replace solvent absorbed by plant. The recirculation flow is about 7 m^3 h^{-1}. This adjustment corresponds to the maximum capacity of possible recirculation so that the juices fall down only in their origin tank without overflowing on the neighbour. Pump is starting when the plant enters on its stage. Raw material mass flow is 15 kg h^{-1}. The barrel is filled until the third of the screw height. Experiments are carried out at ambient temperature. The screw speed is 0.23 rpm. The solid residence time is 2h30, while the solvent can be considered as stagnant (no counter-current).

2.2.3 Solid phase transport

The objective of this test is to determine the flow behaviour of the plant along extractor.

Red plastic tracers were introduced within the plant feed. Their evolution was followed visually. The distance covered (d) by plant according to time can be calculated by multiplying the time (t) with the screw pitch (p) and the screw rotational speed (N):
$$d = t \times p \times N$$
Fig. 3 shows the distance covered by tracers and plant heading front versus time. The evolution of plant heading front is perfectly linear as the distance calculated. Tracers, included further in plant, also follow this evolution. According to the result, the plant transport can be

considered as a plug flow in a first approximation. The average speed of raw plant is 0.23 rpm.

2.2.4 Extraction results

Solid and liquid samples were taken at different times during experience in order to follow the solute concentration evolution. Liquid samples were directly analyzed by HPLC. Each solid sample has been submitted 3 batches of 1 h with fresh solvent. The bulk phase sum gives the solute residual amount contents in sample.

Fig. 4 shows the concentration evolution in various tanks. In each tank, the bulk phase concentration increases in an exponential way. Concentration in first tank rises slowly than in the others because there is a continuous fresh solvent supply. Fig. 5 shows marc depletion in solute along extractor for various experimental times. The solute contained in marc decreases along the extractor. The curve slope decreases according to time. On the other hand, for 150 min and 210 min, there is the same curve. After the establishment of a steady state and although the bulk phase concentration increases, raw material extraction is always the same. The materials balance is calculated at different times. The solute amount in the bulk phase and in the marc is compared with the plant potential. The average spread is 15%. Fig. 6 shows the integrated extraction flux in different tanks. Calculated in bulk phase, this flux is the ratio between concentration and time variation according to the first point. Flux increase during one hour then stabilize towards a given value, in each tank. The establishment of steady state is quite visible in this figure. And it is observed on each tank.

A solute flux decreasing while the liquid concentrates was awaited as in classical continuous extraction. This result leads us to perform batch experiments in order to explain this behaviour of the Vatron Mau unit. The pure diffusion in a 2 L batch stirred reactor and the permeation though a solid bed have been studied. This is the objective of next part.

2.3 Laboratory experiments

2.3.1 Batch extraction experiments

The objective of batch experiments is to measure the global extraction kinetics.

A mass of 100 g of not grinded raw material was inserted in a 2 L reactor, instrumented with a mechanical stirring. The experiment is carried out at ambient temperature. The ratio solid-liquid is stipulated by prior studies. At the initial time, a corresponding volume to used mass was inserted in the reactor. Liquid samples were taken at different times and analyzed by HPLC. Since the global analytic sample volume was small compared to the introduced solvent volume, the measurement was assumed to have no influence on the process. Fig. 7 shows the evolution of the extracted percentage according to time. Data are normalized by the plant potential of plant lot used. The amount extracted tends towards the plant potential. After 1 h, 90 % of solute has been extracted.

These results do not explain the behaviour observed with the Vatron Mau unit. The kinetics batch does not inform about the phenomenon observed on the extraction flux. So, this is not du to the extraction characteristics. Therefore, tests of permeation have been next carried out in order to study the hydrodynamic behaviour.

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2.3.2 Compression cell experiments

Compression cell is a plug placed in a 505 mm length cylinder (Fig. 8). The plug diameter is 85 mm. Raw material is inserted inside the cell on the top. The pressure applied, using the plug, gives different plant densities. On the bottom of the cell different inlets make it possible to feed solvent. There are 5 solvent inlets distant from 30 mm each other and the last one is at 55 mm from the bottom of the cell. This allows to choose the inlet function of the plug position. The solvent outlet is under the cell. The solvent flow was monitored by a diaphragm pump Dosapro Milton Roy (65 L h^{-1} maximum). During experiments, solvent pressure at the outlet pump was measured by a manometer (1-10 bar), and the solvent flow at the cell outlet was measured by weighing (0-500 kg) function of time.

The objective of these experiments is to determine characteristic times of the liquid flow through the solid bed.

Results shown in Fig. 9 were obtained with 400 g of raw material. Different bed densities and different initial states, wet or dried material, have been studied. The density range from 0.371 to 0.542 g cm^{-3} has been chosen in the same order of magnitude of the industrial bundles (0.3 to 0.6 g cm^{-3}).

In each case, the pressure increases until the solvent left the cell. Average solvent exit time is 4 min. When the plant is dried, the pressure goes up to 6 bars then its decrease gradually and tends towards the same pressure to 2 bars. The solvent adsorption may generate a resistance to the flow. In the following test, d = 0.441 g cm^{-3} with wet plant, this pressure increase does not take place. The steady state is reached after 15 to 20 min. At d = 0.542 g cm^{-3} with wet plant, the bed compression bring in an additional resistance to the flow. The pressure decrease is slower than in the others cases.

3 Discussion

3.1 Extractor behaviour

The fig. 10 shows extraction kinetics in the Vatron Mau unit at different experimental times compared to the one obtained in batch. The abscissa time corresponds to the presence duration of plant in Vatron Mau unit, i.e. it is equivalent to the unit length. Data are normalized by the plant potential of plant lot used. The kinetics in Vatron Mau unit slow down with the experimental time until the establishment of steady state. But after 2 h, more than 90 % of solute was extracted in each case.

The Vatron Mau unit is characterized by a plug flow. However, when volume load becomes too important, plant accumulations on the level of solvent distributors are observed. Moreover, the marc discharge zone has the same diameter as the screw. If the screw is filled too much, a plant plug is formed and obstructed the flow. And the more the barrel is filled, the more the time impregnation of the plant is prolonged according to the screw axis. This fact delays the solute extraction.

Compression cell experiments show the importance of plant decompressed. If there are plant packages, the bed leaching is done by preferential channels. All the plant parts will not be accessible to solvent. The global solute extraction is thus less efficient.

Consequently, the solid load can be increased by paying attention to the plant decompressing and by improving the impregnation stage. A maximum loading until half the screw height is recommended.

Leaching tests carried out gave a time characteristic of 20 min. The evolution of the extraction flux (fig.6) shows an establishment time of steady state of 1 h on each tank. Also, for the Vatron Mau unit, the establishment time of steady state is 3h30. During this time, the bulk concentration increased but did not saturate. The solvent flow can be adjusted to maintain a concentration average in tanks. The ratio liquid (L) / solid (S) will be lower than the one used for the batch.

3.2 Batch to continuous

In the batch, the liquid-solid contact is different than in Vatron Mau unit. In the batch, the contact is carried out by immersion whereas in extractor it is by leaching. Then the plant behaviour will be different. More especially as the raw material is very various: bark, root, sheet...

The first step, to pass from the batch to the continuous extractor, is to verify if the raw material can go to the Vatron Mau unit:
- The size of the particles must be sufficiently large so that the plant does not pass through the barrel.
- For the impregnation, the dried plant goes under a strong spray of solvent. It must not fly away or form blocks.
- The wet plant must not stick to the screw or the walls in order to have a correct flow.

The second step is to determine the operating conditions. The solvent and the extraction temperature are supposed chosen by previous studies function of selectivity, safety and economic criterion. The maximum hold up is calculated from the wet material density as plant can dramatically inflate while absorbing solvent. For this calculation in Vatron Mau unit, the constraint to respect in order to ensure a good solid flow behaviour (no plug formed, good repartition of solid) is the height of the solid bed. The solid residence time and the solvent flow rate are derived from desired extraction yield by classical chemical engineering method [8]. This calculation needs the batch extraction results and the equilibrium information as the solvent saturation. It must take in to account the characteristic time of the wetting as measured in the compression cell experiments. Of course, total solid flow rate is fixed by the hold up and the residence time.

4 Conclusions

Continuous extractor is commonly used for liquid-solid extraction from vegetable matrixes. However, its implementation at industrial level requires preliminary laboratory tests in order to ensure the feasibility of the process and get element to evaluate economic impact. This also involves the search of the optimal extraction conditions, in order to maximize the efficiency of the process.

As it has been said, each couple material-solvent shows different behaviour and specific studies are needed. Furthermore, we also show that the industrial equipment used is of great importance and need the acquisition of specific information. The ideal continuous solid-liquid contactor which allows direct transposition from pure batch diffusion study does not exist in industrial context.

In this work, transposition from batch to continuous solid-liquid extraction is studied. The extraction in batch allows choosing solvent, liquid-solid ratio, operating temperature and contact time. The study of Vatron Mau unit has revealed the necessity of other data.

The preliminary test can be carried out at laboratory scale. A small amount of plant is necessary to study the size distribution, the impregnation stage, and wet plant behaviour with steel. The following tests are carried out in batch: kinetic extraction determination and bulk

phase saturation. Some tests in Vatron Mau unit remain necessary to adjust the operating conditions.

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The solid-liquid extraction of active principle from raw plant substrate is studied in a specific continuous counter-current extractor. A methodology including preliminary laboratory tests is presented in order to ensure its implementation at industrial level.

Figure 1. Vatron Mau picture (courtesy of Pierre Fabre Inc.).
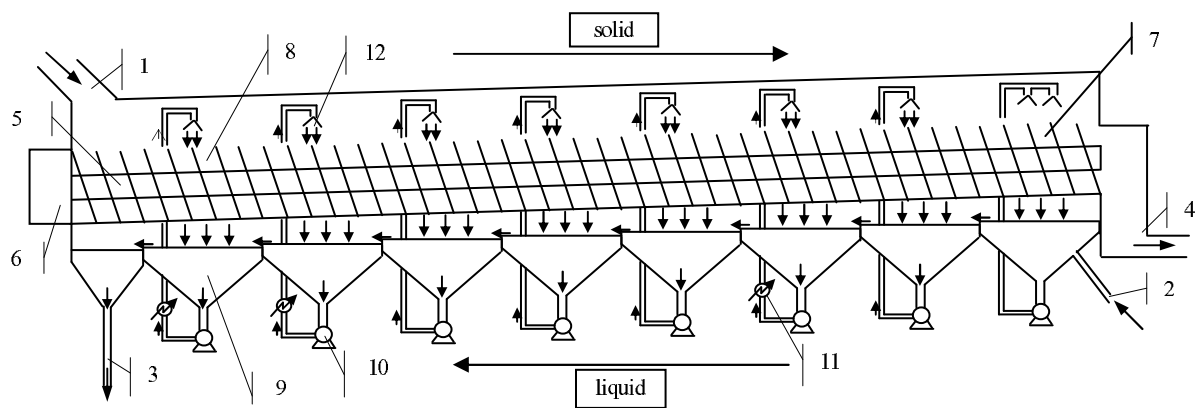
Figure 2. Scheme of Vatron Mau: (1) plant entrance; (2) solvent inlet; (3) solute exit; (4) marc exit; (5) screw; (6) motor; (7) drainage zone; (8) percolation section; (9) tank; (10) pump; (11) heat exchanger; (12) solvent distributor.
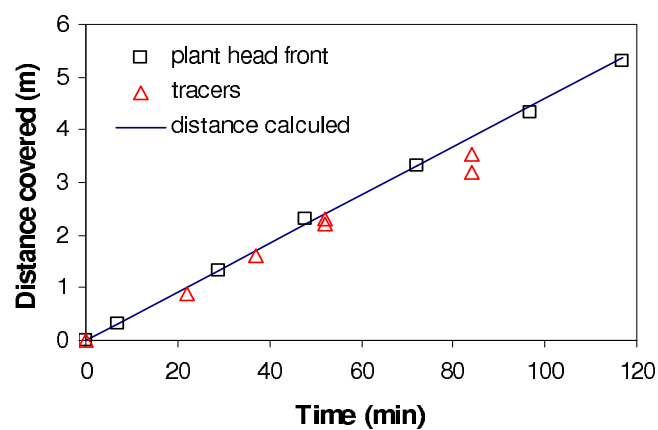
Figure 3. Tracers and plant advancement.
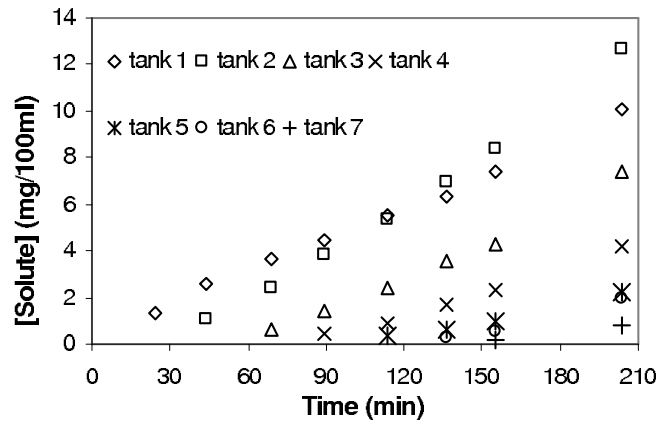
Figure 4. Evolution of solute concentration in the extract enriched.
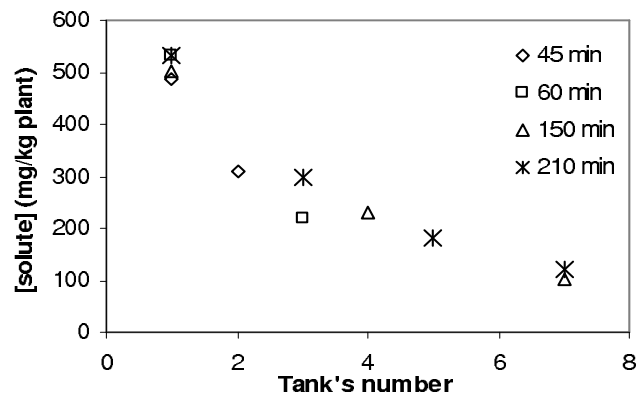
Figure 5. Evolution of solute concentration in the marc.
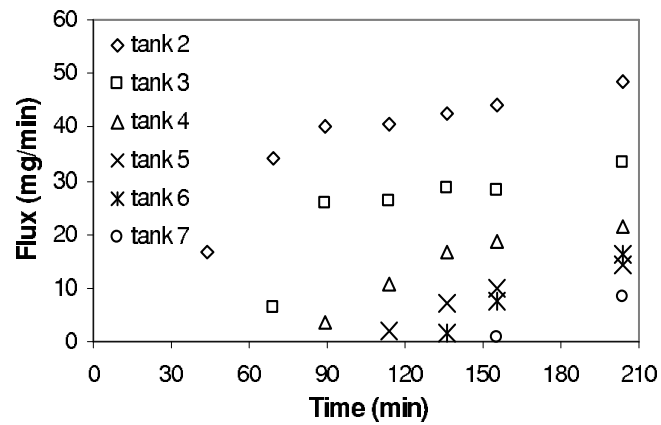
Figure 6. Evolution of extraction flux in the bulk phase.
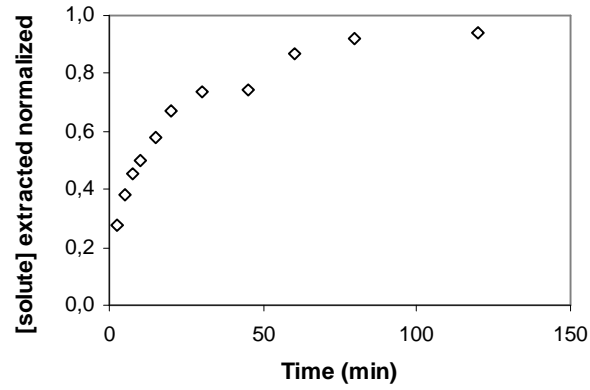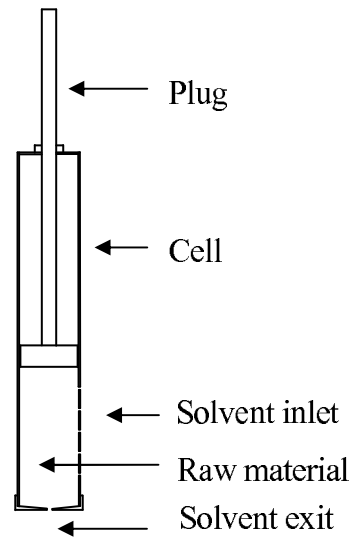
Figure 7. Batch kinetics.

Figure 8. Picture of compression cell.
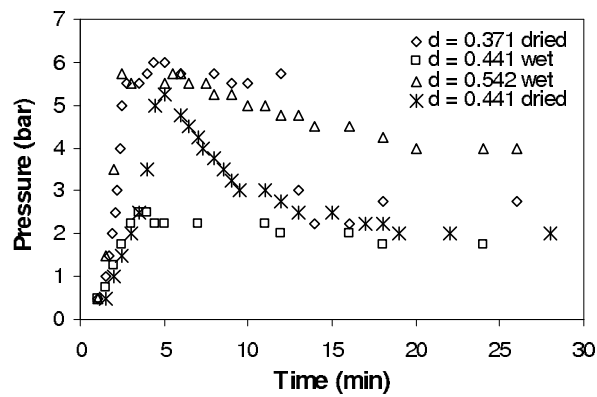

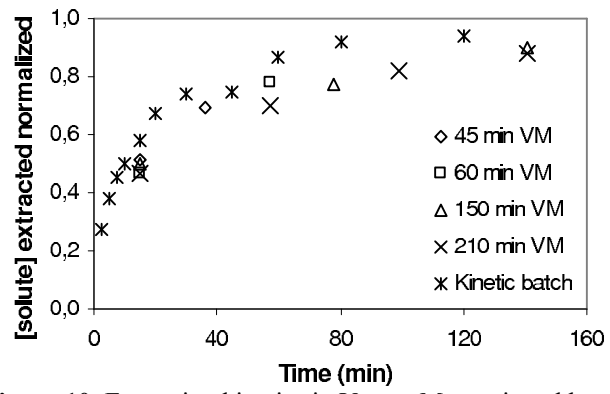**Figure 9.** Evolution of pressure at different densities

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Figure 10. Extraction kinetics in Vatron Mau unit and batch.